Electrochemical Passivation of Niobium in KOH Solutions

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Electrochemical formation and dissolution of passive films on niobium surfaces were studied in various concentrations of KOH solutions using the open-circuit potential and potentiodynamic techniques. Potentiodynamic *I/E* profiles indicated that the electrolyte concentration strongly affects the active/passive transition, as well as the values of the passivation potentials and critical currents. At higher KOH solution concentrations, after passivation of the electrode surface in the first positive cyclic voltammetry scan, reactivation processes were monitored in the reverse scan. Formation of passive films is a diffusion-controlled process only for higher sweep rates. Cathodic pretreatment of niobium electrode affects the chemical structure and oxide composition of passive films. Corrosion measurements have shown that at higher KOH concentrations the passive film is rapidly attacked and the corrosion resistance of Nb electrode is drastically diminished.

INTRODUCTION

Electrochemistry of niobium is an attractive research field because this metal has a high mechanical and corrosion resistance and wide application as a stable construction material in many fields of technology. It has been identified as the preferred construction material for the first reactors in the space power system programs. Niobium is totally hypoallergenic and the safest metal that human body can tolerate. It is frequently used in artificial joints, plates, pacemakers and dental implants.

The Nb corrosion stability in most aqueous solutions usually considered highly corrosive, such as mineral acids, organic liquids and organic acids, is due to a natural oxide film on its surface. Notable exceptions are dilute strong alkalis, hot concentrated mineral acids and hydrofluoric acid, which rapidly attack the metal. Corrosion resistance of Nb can be enhanced by supplemental electrochemical formation of passive and/or anodic oxide films. This actualizes investigations of niobium behavior in alkaline solutions, involving self-passivation and chemical stability of the oxide film, either polarized or non-polarized.

Thus far, a great number of papers have been published concerning the passive behavior of Nb in acid and salt aqueous solutions.[1–4] However, a relatively small number of papers address passive behavior in dilute alkaline solutions.[5–7] Only a few studies have been published on the stability and dissolution of passive films of Nb in concentrated NaOH and KOH solutions.[8,9] In all these studies, less attention has been paid to the surface preparation and the influence of cathodic pretreatment of the Nb electrode on potentiodynamic *I/E* profiles. The main reason for the lack of these electrochemical data is the changeability of the surface chemical composition, especially at higher cathodic potentials. During cathodic

polarization, niobium can be embritlled in salts that hydrolyze even at low concentrations (5 %) of sodium or potassium hydroxide.[10]

The purpose of the present study is a more systematic investigation of the influence of the initial electrochemical conditions on the passive film formation and its dissolution on Nb surfaces in KOH solutions of various concentrations. In addition, the corrosion resistance of the Nb electrode was also studied.

EXPERIMENTAL

Electrodes

The working electrode was prepared from annealed 99.8 % niobium rod (Alfa Aesar, Johnson Matthey Company). The Nb discs were glued to the inside of a Pyrex glass tube with epoxy resin to provide an electrode exposed surface area of 0.316 cm^2. The electrode was then mechanically polished with emery paper 600, carefully rinsed, and finally ultrasonically cleaned in ethyl alcohol.

A Pt grid with a large surface area was used as a counter electrode, and an Hg/HgO/1mol dm^{-3} KOH electrode served as reference. All the measured potentials were referred to the standard hydrogen electrode (SHE).

Electrochemical Cell

Classical Pyrex glass cell with separate compartments for auxiliary and reference electrodes, as well as a Luggin capillary and an inlet and outlet for bubbling inert gas was used. Prior to each experiment, the solution in the cell was initially de-aerated by flowing argon gas through a fritted bubbler for at least 30 min before the run. During the run, the gas flow through the solution was disconnected and was passed above the solution.

Solutions

Aqueous solutions of potassium hydroxide with concentrations of 0.1, 1, 2, 5 and 10 mol dm^{-3} were prepared from KOH (Merck, extra pure) with triply distilled water. After each measurement, the electrolyte in the cell was exchanged in order to avoid potential formation of soluble species.

Apparatus

A HEKA Model IEE 488 potentiostat/galvanostat connected to a PC was used for electrochemical and corrosion measurement.

RESULTS AND DISCUSSION

Open Circuit Potential (OCP)

In case of Nb handled in air, the electrode surface is always covered spontaneously by a natural oxide film, predominantly Nb$_2$O$_5$ as the outer layer and a small part

of NbO$_2$ as the inner layer.[7] After mechanical polishing, the electrodes were quickly transferred to the electrochemical cell, taking the immersion moment as zero time. Variations of OCP are given in Figure 1.
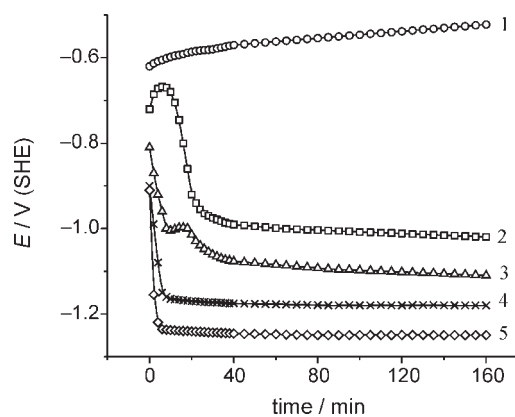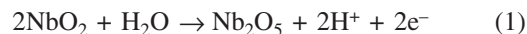

Figure 1. OCP potential *versus* time of an Nb electrode at various KOH concentrations: 1) 0.1 mol dm^{-3}, 2) 1 mol dm^{-3}, 3) 2 mol dm^{-3}, 4) 5 mol dm^{-3} and 5) 10 mol dm^{-3}.

For 0.1 mol dm^{-3} KOH, the small anodic shift with time indicates a slight thickening of the natural oxide film. During this process, the part of NbO$_2$ in natural oxide film is oxidized to Nb$_2$O$_5$.

$$2NbO_2 + H_2O \rightarrow Nb_2O_5 + 2H^+ + 2e^- \qquad (1)$$

In 1 mol dm^{-3} KOH, first the OCP increases faster as a result of faster oxidation of NbO$_2$ to Nb$_2$O$_5$, showing a potential of about $-$ 0.66 V, and then, after 160 min, decreases to the steady state potential at $-$ 1.03 V. The potential change in cathodic direction could be attributed to dissolution of the natural oxide film. It is evident that two processes occurred in 1 mol dm^{-3} KOH: first a slight thickening and then thinning of the natural oxide film. At higher KOH concentrations, the electrode potential was shifted only in cathodic direction, indicating that the oxide film was subject to continuous dissolution. The extremely fast potential jump in cathodic direction, shortly after Nb was dipped in 5 mol dm^{-3} and 10 mol dm^{-3} KOH, resulted from faster dissolution of the natural oxide film in the early stage and the steady state potential was achieved in a shorter time. The thinning of the natural oxide film was monitored ellipsometrically, but unfortunately the ellipsometric data cannot give a reliable answer to whether the natural oxide film was completely dissolved, or which quantity of it was dissolved.

According to Badawy *et al.*,[9] the most probable dissolution reaction in aggressive NaOH solutions ($c_{NaOH} >$ 2 mol dm^{-3}) may be written as:

$$3Nb_2O_5 + 6OH^- \rightarrow 6NbO_3^- + 3H_2O \qquad (2)$$

Cyclic Voltammetry

The electrodes previously subjected to different KOH solutions (experiments represented in Figure 1) were studied by cyclic voltammetry.

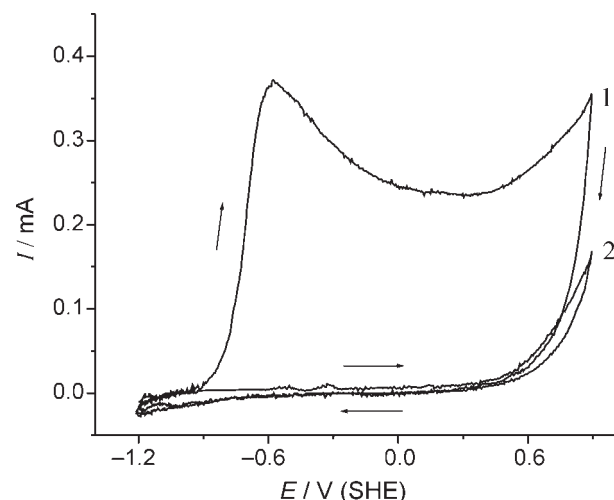Figure 2 illustrates the cyclic voltammograms for the Nb electrode in 1.0 mol dm^{-3} KOH solutions.

Figure 2. Cyclic voltammograms of Nb registered in 1 mol dm^{-3} KOH, starting from –1.2 V; 1) 1st cycle, 2) 2nd cycle ($v = 50$ mV/s).

The potential sweep was initiated at –1.2 V. In the first positive scan, an active dissolution region followed by the passivation process was observed.

As suggested in Ref. 1, metal dissolution in the active region occurs via the reaction:

$$Nb \rightarrow Nb^{5+} + 5e^- \qquad (3)$$

while in the passive region the film thickness grows according to the reaction:

$$2Nb + 5H_2O_5 \rightarrow Nb_2O_5 + 10H^+ + 10e^- \qquad (4)$$
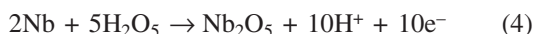
The progress of each reaction depends on the concentration of KOH, surface pretreatment and initial electrochemical conditions.

No cathodic peak was observed in the first reverse cycle, up to –1.2 V. The passive film formed in the 1th positive scan cannot be cathodically reduced. In the second and next subsequent cycles, large current plateaus, with values close to zero, were recorded for both forward and reverse scans. It is evident that after the first cycle the Nb electrode remained passive in the whole investigated potential region and the formed passive film blocked all possible redox reactions of Nb/passive film/electrolyte at the interface.

Effect of KOH Concentration

Effects of the KOH concentration (0.1 – 10 mol dm^{-3}) on the potentiodynamic curves of the Nb electrode at room temperature, for the sweep rate from 10 to 200 mV/s, were investigated. When increasing the KOH concentration, big changes were observed in the voltammogram shape, especially in the reverse cycles. Figure 3 shows voltammograms for the 1st forward and reverse cycles registered on the Nb electrode when maximum anodic current in the active region was much higher than in 1.0 mol dm^{-3} KOH.

In the reverse scan, a well-distinguished reactivation process is observed. The effects caused by increasing KOH concentrations can be interpreted in terms of enhanced solubility of Nb oxides.

Inspection of the data recorded for all investigated concentrations reveals that the height of the maximum anodic current I_m and its corresponding primary passivation potentials E_p are shifted towards more negative potential values at increased KOH concentrations. Such behavior can be seen in Figure 4 where the plots log c – E_p and log c – log I_m are given.

For both graphics, the relations are not linear and show two slopes. Both graphics indicate two different mechanisms (electrochemical passivation and dissolution of passive films) occurring at the electrode surface. The former is predominant in solutions up to a concentration of 2 mol dm^{-3} KOH, while the letter prevails in solutions of a concentration higher than 2 mol dm^{-3} KOH.
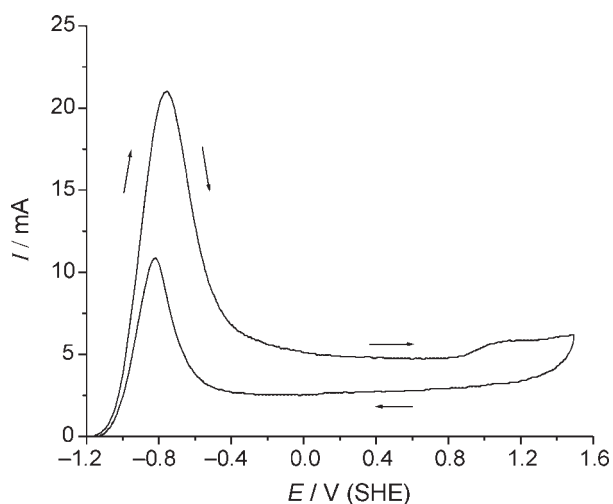

Figure 3. Cyclic voltammograms of Nb registered in 10 mol dm^{-3} KOH, starting from –1.2 V ($v = 20$ mV/s).

The anodization coefficient α is calculated from the steady state current density j_s, according the equation:

$$\alpha = \frac{j_s \cdot M}{z \cdot F \cdot v \cdot \delta_{ox}} \qquad (5)$$
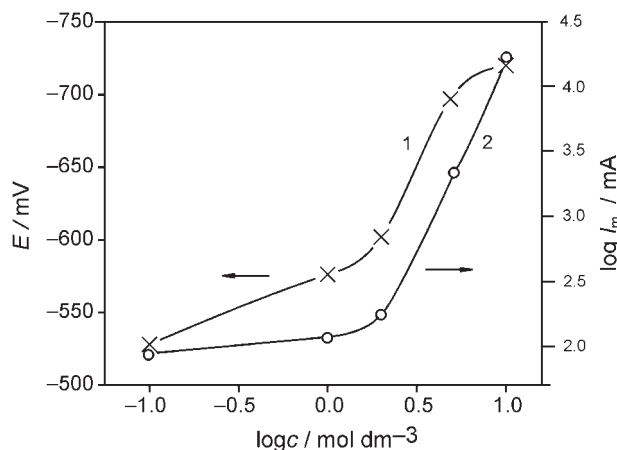
Figure 4. Dependence of the primary passivation potential E_p and maximum anodic current I_m on the KOH solution concentration. Values for E_p were taken for $v = 20$ mV/s.
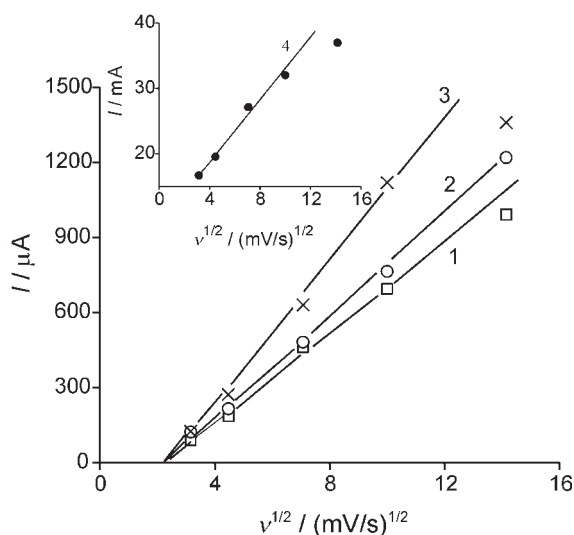

Figure 5. Dependence of the maximum anodic current on the square root of the sweep rate of the Nb electrode in: 1) 0.1 mol dm^{-3} KOH, 2) 1.0 mol dm^{-3} KOH, 3) 2 mol dm^{-3} KOH and 4) 10 mol dm^{-3} KOH.

where M is the oxide molecular weight, z is the number of electrons exchanged, F is the Faraday constant, v is the potential sweep and δ_{ox} is the density of the oxide. For the assumed passive film of Nb$_2$O$_5$, $M = 265.8$ g/mol, $z = 10$ according to reaction (4) and $\delta_{ox} = 4.47$ g/cm^3. The same values are also given in Ref. 5. For the constant ratio $M/z \cdot F \cdot \delta_{ox}$ for all investigated concentrations and sweep rates, the value of 6.16×10^{-5} cm^3 C^{-1} was determined. As seen from cyclic voltammograms, the calculated values of α vary from 1.82 nm/V to 4.0 nm/V depending on the KOH concentration and sweep rate. These big differences should originate from the predominating process – electrochemical passivation or dissolution of passive films. The values of α generally show that the oxides grow thicker in KOH than in acidic electrolytes, since OH$^-$ adsorption of the oxide/electrolyte interface hinders incorporation of any other anions, enhancing ion conduction and transfer through the oxide film.[5]

Effect of Potential Sweep Rate

Data on the potential sweep rate from $v = 10$ to $v = 200$ mV/s confirm the strong dependence of this effect on film formation and its dissolution. The maximum anodic current I_m and the steady-state current are dramatically increased with increasing sweep rate. On the other hand, the primary passivation potential is slightly shifted to a more anodic potential. Figure 5 shows the plot of I_m *versus* the square root of v for various KOH concentrations.

At 0.1 mol dm^{-3} and 1 mol dm^{-3} KOH, the plot is in straight lines and the formation of Nb oxide passive layers is a diffusion controlled process. At 2 mol dm^{-3} and 10 mol dm^{-3} KOH, the plot is linear for the low sweep rate. At the high sweep rate, deviation from straight line indicates that the process is not purely diffusion controlled. At 5 mol dm^{-3} KOH, no mathematical function can be established as a result of possible competition of

various processes on the electrode surface. The nature of the passive film formed from 0.1 mol dm^{-3} to 2 mol dm^{-3} KOH seems to be different from that at 10 mol dm^{-3} KOH. The transition of these two kinds of layers is more accentuated at 5 mol dm^{-3} KOH. At high sweep rates, dissolution of the oxide film may compete with the rate of its formation (dissolution/passivation mechanism). The oxide film formed at high sweep rates might have higher hydration content and builds OH$^-$ bridges.[11] Consequently, the more hydrated oxide is expected to have lower density and a higher dielectric constant. In addition, it was recently found that the films formed at different sweep rates have considerably different porosities.[12] All these data could explain the deviation from linear plot at high sweep rates.

Effect of Cathodic Pretreatment

At initial cathodic potential of –1.5 V, where a considerably cathodic current is observed, evolution of hydrogen occurs on the electrode surface. Under cathodic polarization, a part of hydrogen, which is generated on the Nb electrode, is absorbed on the electrode surface and when its amount becomes large, a niobium hydride will be formed. This process may be expressed by the equation:
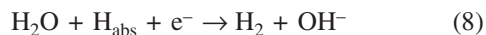
$$H_2O + e^- \rightarrow H_{ads} + OH^- \qquad (6)$$
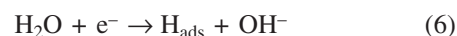
A part of the absorbed hydrogen penetrates into the surface forming niobium hydride:[7,8]

$$Nb + H_{abs} \rightarrow NbH_{(1-x)} \qquad (7)$$
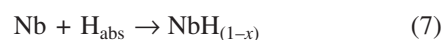
where $x < 1$. Niobium hydride is known to have a wide non-stoichiometric composition.[13] The other part of ab-

sorbed hydrogen is liberated by electrochemical desorption:

$$H_2O + H_{abs} + e^- \rightarrow H_2 + OH^- \qquad (8)$$

Therefore, the oxide films existing on the Nb electrode affect its behavior during cathodic polarization. Based on the results of XPS analyses, Sugimoto et al.[7] have shown the existence of an oxyhydroxide in which the oxidation state of Nb is slightly lower than Nb^{5+}.

Figure 6 displays the potentiodynamic curves for the first and second cycles on the Nb electrode cathodically pretreated for 15 min at a potential of –1.5 V before the run.
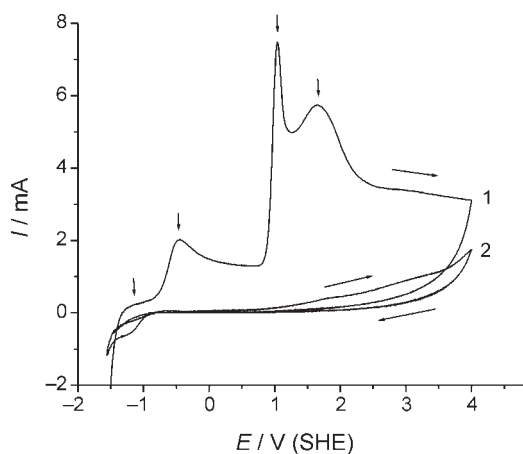

Figure 6. Cyclic voltammograms of Nb cathodically pretreated for 15 min at –1.5 V in 2 mol dm^{-3} KOH before the run; 1) 1st cycle, 2) 2nd cycle (v = 200 mV/s).

In the potential region from –1.5 V to 4 V, four distinctive anodic peaks are observed in the first forward cycle. These four peaks are more pronounced when increasing the sweep rate. In the first reverse scan in Figure 6, non-corresponding cathodic peaks were monitored. In the second cycle, the existence of a large current plateau in both directions, without appearance of any peak, indicates that the Nb electrode remained passive in the whole potential range investigated. Recently, B. X. Huang et al.[6] demonstrated facile formation of a stable passivation film on the Nb electrode at 0.15 mol dm^{-3} NaCl and 0.1 mol dm^{-3} NaOH. Starting from the cathodic potential of –1.3 V Ag/AgCl, with notable current density, their voltammogram in the first positive scan consisted of four anodic peaks, generally poorly defined. In the potential region from –1.3 to 1.4 V they claimed the existence of four oxides: NbO, NbO_2, Nb_2O_5 and $Nb_2O_5 \cdot H_2O$. Their results are consistent with ours, but there is a significant difference in peak positions. Comparative analyses of voltammograms obtained with or without cathodic pretreatment have shown that cathodic pretreatment changes the chemical composition and ratio of oxides existing on the electrode surface. In alkaline solutions, pH about 14,

the equilibrium potentials for the reactions between Nb and its oxides are highly cathodic: Nb/NbO (–1.57 V), Nb/NbO_2 (–1.46 V) and NbO_2/Nb_2O_5 (–1.128 V).[14]

Corrosion Resistance

The corrosion resistance of Nb electrode, at various KOH concentrations, was studied using the Tafel plots and polarization resistance measurements. Tafel plots were recorded in the potential region within –300 and + 300 mV of corrosion potential. To avoid possible electrode reactions during the polarization, polarization resistances were recorded in a shorter potential range, within –20 and +20 mV of corrosion potential.

Some representative examples of Tafel plots are given in Figure 7.

For all investigated concentrations, from 0.1 to 10 mol dm^{-3} KOH, the cathodic and anodic polarization curves followed an almost linear Tafel behavior, mainly resulting from hydrogen evolution or metal dissolution. The corrosion current was obtained by extrapolating the Tafel lines to zero overpotential. Table I gives the corrosion parameters derived from the Tafel plot and corrosion resistance derived from polarization measurements.

Cathodic Tafel slopes vary from 110 to 150 mV/decade, indicating exchange of one electron during the cathodic reaction. Anodic Tafel slopes vary from 62 to 120 mV, indicating exchange of two electrons at lower KOH concentrations and one electron at higher KOH concentrations. It is noteworthy that some anomalous values of Tafel slopes probably originated from various mechanisms of metal dissolution, depending on the KOH concentration. The explanation of this behavior involves the basic assumption that some part of the applied voltage is consumed across the oxide and is hence not available to assist the charge transport at the electrode/solution interface. There is a barrier within the oxide film that moderates the transport of electrons through
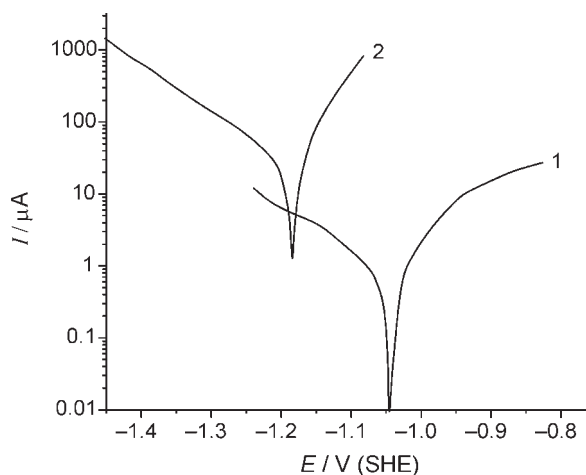

Figure 7. Tafel plots recorded on Nb in: 1) 1 mol dm^{-3} KOH, 2) 10 mol dm^{-3} KOH.

TABLE I. Corrosion parameters of the Nb electrode at various KOH concentrations

KOH	I_{corr}	R_p	Corr. rate
mol dm^{-3}	µA cm^{-2}	kΩ cm^{-2}	µm year^{-1}
0.1	0.99	78.89	7.1
1.0	2.42	61.39	17.0
2.0	4.24	39.17	33.2
5.0	19.87	14.24	104.0
10.0	70.25	3.13	498.0

the film and application of higher overvoltage is necessary for the reaction to occur.

Corrosion data given in Table I allow the conclusion that there is a big change in corrosion parameters between 0.1 and 10 mol dm^{-3} KOH, indicating a marked enhancing rate of electrode dissolution at higher KOH concentrations. The barrier properties of natural and passive oxide films on the electrode surface are not sufficiently protective in comparison with H$_2$SO$_4$ solutions. For example, the corrosion rate in 0.1 mol dm^{-3} H$_2$SO$_4$ is 8.6 µm year^{-1}, while in 10 mol dm^{-3} H$_2$SO$_4$ it is 11.5 µm year^{-1}, Ref. 15. Corrosion data showed that niobium metal could not be recommended for construction materials in solutions of higher KOH concentrations.

CONCLUSIONS

The potential-time profiles at OCP reveal that at 0.1 mol dm^{-3} KOH a slight thickening of the natural oxide film on the Nb surface occurs, while at higher concentrations this film is sinking under continuous dissolution.

The I/E profiles reveal the active/passive transition of the metal electrode and two different mechanisms of electrochemical passivation, and dissolution of passive films. The passive films formed at 0.1 mol dm^{-3}, 1 mol dm^{-3} and 2 mol dm^{-3} KOH differ from those formed at 5 mol dm^{-3} and 10 mol dm^{-3} KOH.

Passive films of the cathodically pretreated Nb electrode consist of four various oxides of thermodynamically most probable composition NbO, NbO$_2$, Nb$_2$O$_5$ and Nb$_2$O$_5$ · H$_2$O.

The corrosion data reveal that the dissolution of metal surface is greatly affected by alkali concentrations and that at higher KOH concentrations passive films posses less corrosion resistance with weaker protective properties.

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SAŽETAK

Elektrokemijsko pasiviranje niobija u otopinama KOH

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Elektrokemijsko nastajanje i otapanje pasivnih filmova na površini niobija proučavano je u vodenim otopinama KOH raznih koncentracija mjerenjem promjene potencijala otvorenog kruga i uporabom potenciodinamičkih tehnika. Oblik potenciodinamičkih I/E krivulja pokazuje da koncentracija elektrolita bitno utječe na aktivni/pasivni prijelaz, kao i na vrijednosti potencijala pasiviranja i gustoće struje. Kod viših koncentracija otopina KOH, nakon pasiviranja elektrodne površine u prvom voltametrijskom ciklusu, registrirani su reaktivacijski procesi u povratnom ciklusu. Stvaranje pasivnih filmova je proces kontroliran difuzijom samo kod nižih brzina cikliranja potencijala. Katodna predobrada elektrode niobija bitno utječe na kemijsku strukturu i sastav oksida u pasivnom filmu. Korozijska su mjerenja pokazala da je pri višim koncentracijama KOH pasivni film kemijski nestabilan i korozijska otpornost Nb elektrode drastično opada.